LIQUEFACTION REACTIVITY MEASUREMENTS ON ARGONNE PREMIUM COAL SAMPLES

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ABSTRACT

Liquefaction reactivities for a suite of 4 coals from the Argonne Premium Coal collection have been measured in tubing bomb batch reactors. The coals span a rank range from low volatile through medium and high volatile bituminous to subbituminous. The coals were liquefied in 4 different vehicles (solvents) namely naphthalene, phenanthrene, tetralin, and 1-methylnaphthalene at 698 K (425 C), 6.2 MPa (900 psi) initial hydrogen pressure, and at 5 and 40 minutes residence times. The rate and extent of conversion to THF- and toluene-solubles was measured, and gas make and hydrogen consumption quantified directly. The data show that, for purposes of reactivity comparisons, conversion to toluene-solubles provides the most appropriate data for relative reactivity ranking purposes. The Wyodak subbituminous coal was found to have the highest rate of reaction of the four coals investigated, while the Illinois #6 high volatile bituminous coal exhibited the greatest extent of reaction (conversion to THF- and toluene-solubles).

BACKGROUND

Measurement and correlation of coal reactivity under coal liquefaction conditions has been investigated for many years. Most studies in this area have attempted to find a single parameter or group of parameters capable of correlating fundamental physical, chemical, and geochemical coal properties with the degree of conversion to solvent soluble products under some set of standard reaction conditions (1-6). The relationship between coal organic and inorganic composition and hydrogenation reactivity has been extensively researched by several groups of investigators, most notably by Fischer et al., Given et al., and more recently by Baldwin et al. (7-21).

The purpose of this study was to examine the reactivity of 4 different coals in four different liquefaction vehicles so that the effect of solvent type on coal reactivity could be elucidated. The goal of this portion of the study was to determine the effect of liquefaction vehicle on the absolute and relative reactivities of four coals representing a broad rank range.

EXPERIMENTAL

Four coals from the Argonne Premium Coal collection were liquefied in four different vehicles. The coals employed for this study were:

- Wyodak subbituminous
- Illinois #6 high volatile bituminous
- Upper Freeport medium volatile bituminous
- Pocahontas low volatile bituminous

Properties of these coals are available from Argonne National Laboratory. The vehicles (solvents) employed consisted of both donor and non-donor species:

tetralin
1-methylnaphthalene
phenanthrene
naphthalene

Experimental runs were carried out in a tubing bomb microautoclave reactor system at 698 K (425 C), 6.2 MPa (900 psi) initial hydrogen pressure, and for reaction times of 5 and 40 minutes. Data on the conversion of each coal in each solvent to gas, THF-, and toluene-solubles was collected. Details on the procedures utilized have been described elsewhere (22).

DISCUSSION OF RESULTS

Effect of Vehicle on Liquefaction Reactivity

The objective of this study was to determine the reactivity of these four coals under identical reaction conditions, but in different pure solvents. Conversion to both THF- and toluene-solubles was measured. Our previous work has indicated that THF-soluble data provides a poor measure for liquefaction reactivity while toluene solubility data gives excellent correlation between coal properties and coal reactivity (23).

Data from the liquefaction of these four Argonne Premium coal samples in each of the four solvents are shown graphically in Figures 1 through 4. Figures 1 and 2 present the results for conversion of the coals to toluene-solubles at 5 and 40 minutes reaction time, while the data for THF-solubles is presented in Figures 3 and 4. As indicated in Figures 1 and 2, the absolute magnitude of conversion to toluene-solubles is not a strong function of the choice of liquefaction vehicle as long as the type of vehicle (donor vs. non-donor) remains unchanged. Hence the absolute value of the conversions to toluene-solubles are remarkably similar in phenanthrene, naphthalene, and 1-methylnaphthalene. Switching from a non-donor to a hydrogen donor solvent brings about an increase of 20 to 30% in the absolute value of the conversion to toluene-solubles at both 5 and 40 minute reaction times. This observation simply reflects the difference in rate that exists due to the difference in hydrogenation mechanisms in the two solvent systems. In the one case (the donor solvent tetralin) hydrogen needed to stabilize free radicals or to directly attack and cleave strong bonds in the coal matrix can be supplied directly from a hydroaromatic. When a non-donor is used however, the mechanisms of hydrogen transfer are less direct, and involve hydrogen shuttling and/or formation of radical species by reaction of solvent molecules with molecular hydrogen which then can serve as radical cappers and active bond fission promoter as illustrated by McMillen et al. (24).

While the absolute magnitudes of the conversions are functions of solvent, the relative reactivity rankings are <u>not</u> affected by the nature of the solvent if care is exercised in selecting an appropriate data set for purposes of making reactivity comparisons. Different defininitions can be used for reactivity depending on the nature of the processing property of interest. From a rate processes perspective, the coal with the highest reaction rate would be judged to be the most reactive, while from a static point of view the ultimate extent of conversion to either THF- or toluene-solubles would be the appropriate measure of reactivity. In all cases regardless of vehicle type, the Wyodak subbituminous coal was the most reactive from a kinetic standpoint (based on the rate of conversion to toluene-solubles). In terms of ultimate conversion (extent of conversion to toluene-solubles), the Illinois #6 high volatile bituminous coal was the most reactive, followed by the Wyodak subbituminous coal and the medium and low volatile bituminous coals. These data show clearly that, over a broad range of coal types and reaction times, the nature of the liquefaction vehicle is not a major factor in determining the inherent reactivity of the coal. Figures 3 and 4 display the problems encountered when attempting to utilize data on conversion to THF-solubles as the measure of liquefaction reactivity. As shown, the reactivity rankings are not the same as for the toluene-soluble data set. Further, the relative reactivities of the four coals in terms of both rate and extent of reaction now <u>are</u> a function of the type of liquefaction vehicle employed. The indicated solvent effects and reactivity reversals exhibited by the THF-solubles data make it extremely difficult to draw any concrete conclusions regarding the effect of coal properties on reactivity.

ACKNOWLEDGEMENTS

This work was performed under sponsorship of the United States Department of Energy, Grant no. DE-FG22-85PC80907.

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FIGURE 1

Toluene Solubles, 5 Minute Reaction Time

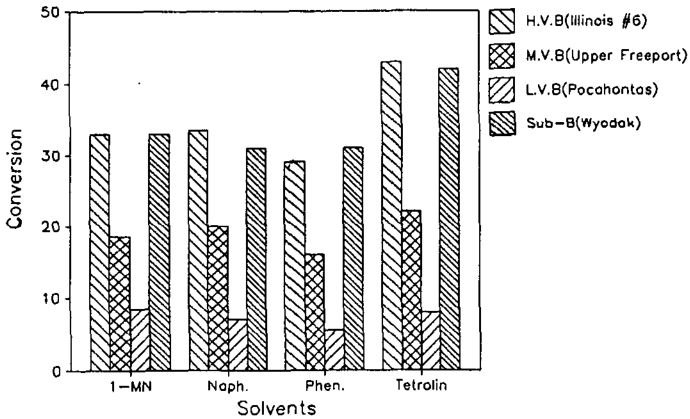

FIGURE 2

Toluene Solubles, 40 Minute Reaction Time

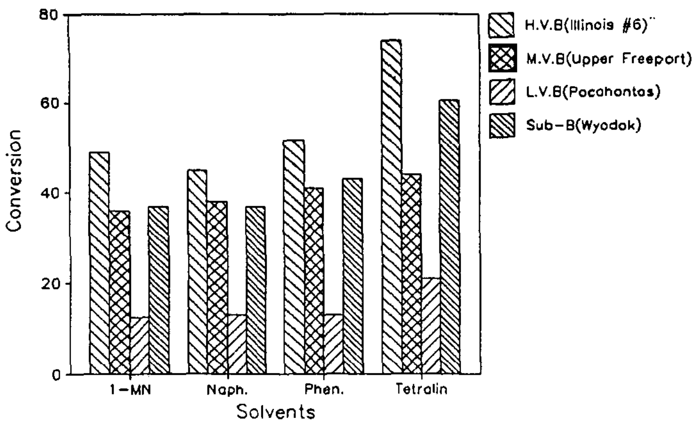

FIGURE 3

THF Solubles, 5 Minute Reaction Time

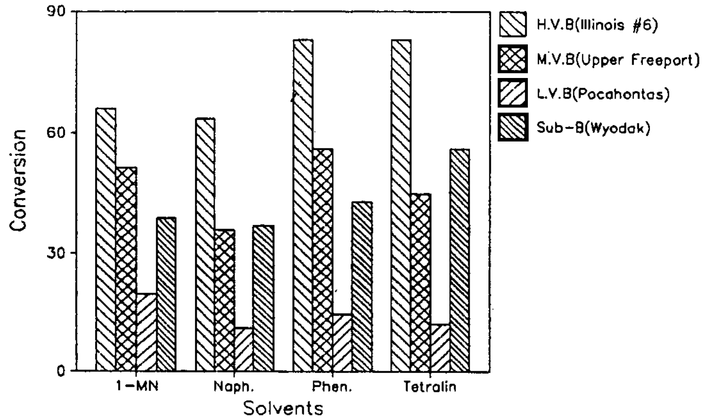

FIGURE 4

THF Solubles, 40 Minute Reaction Time